11

SPECTROSCOPIC CONSTANTS OF MOLECULES I ON THE GROUND STATE FREQUENCIES OF DIATOMS OF THE TYPE XX

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(*Received for publication, December 19, 1953*)

ABSTRACT. The theoretical evaluation of the spectroscopic constants of molecules by quantum mechanics has been retarded due to the difficulties in calculations. In the present and the succeeding papers the authors propose to discuss the existing relations and to suggest new ones—empirical or semi-theoretical—between the spectroscopic constants of molecules. A new unit for "10^5 dynes/cm." *viz.* "Des." after the pioneer worker Deslandre is proposed.

An improved form of Matuyama-Clark relation connecting the ground state frequencies of diatoms (diatomic molecules) formed of the same element has been suggested. The relation is $\log \omega_e = g - h \log n^2 V$, where n is the total quantum number of the valence electrons, V the ionisation potential and g and h are constants for each group. Values for FrFr, GeGe, SnSn, PoPo and AtAt have been predicted.

GENERAL INTRODUCTION

The explanation of hydrogen molecule on wave mechanics by Heitler and London (1927), and the refinements by later workers, placed the valence theories on a solid foundation and it became possible to calculate theoretically the spectroscopic constants of H_2. However, except for the simplest cases the theoretical discussion of molecules deals with the problem of a system consisting of rather large number of particles (electrons and nuclei). There is hardly any possibility of solving such problems rigorously. To arrive at an approximate solution various factors have to be neglected. According to the type of approximation used, we are led to different valence theories. Often the approximations are very questionable and the results obtained can only be called 'daring approximations'. So far as numerical magnitudes are concerned, the calculations are almost hopelessly complicated for the heavier molecules. As Coulson (1952) remarks "It has laughingly been said that calculating the dissociation energy of a heavy molecule is like weighing the captain of a ship by determining the difference in displacement of his ship when he is, or is not, on board."

Attempts have been made in the past to obtain empirical correlations between different molecular constants, such as force constant, internuclear distance etc. Some of the well-known empirical formulae are due to Brige (1925), Mecke (1925), Morse (1929), Clark and his collaborators (1934-1952),

Allen and Longair (1935), Badger (1934, 1935), Huggins (1935, 1936), Sutherland (1938, 1940), Linnett (1940, 1942), Gordy (1946), Guggenheimer (1946), Wu and Chao (1947) and others.

It is the purpose of the present and the succeeding papers to discuss the existing relations and to suggest new ones—empirical or semi-theoretical. The methods will be applied to the prediction of undetermined constants wherever possible.

It is expected that the present method of approaching the problem of spectroscopic constants may prove useful, in encouraging experimental and theoretical developments. From the practical standpoint, some incentive may be given to the task of verification or otherwise of predicted values. Further, a more careful determination of such constants which are found to be empirically anomalous would be advisable (e.g. vibration frequencies of FF, PN, AsN etc.) It is interesting to note that often two independent empirical methods lead to the same results.

On the theoretical side, as mentioned above, progress by the rigorous methods of quantum mechanics has been retarded by difficulties of calculation, and empirical methods may, therefore, be useful. The present trend indicates that the theory will advance more along a semi-empirical, rather than a purely theoretical approach. Some of the empirical relations may serve as hand holds by which the theoretician can climb to more commanding positions.

NOTATION AND SYMBOLS

Clark (1935 *b*) has suggested the use of the term "di-atom" as a short form of the somewhat cumbersome "diatomic molecule" and he has advanced several reasons in support of his suggestion. Though his suggestion has not gained general currency, it is found that it is very convenient and will be used.

Similarly following Clark a homonuclear diatomic molecule will be denoted by XX instead of the conventional X_2. Walsh (1951) has also used the same symbol.

Clark has divided the molecules into 'periods' which are designated as KK, KL, KM, LL, LM etc., the letters indicating the closed electronic shells of the component atoms. Thus CO is (KK), AlO is (KL) etc. This notation has since been followed by several authors and it will also be followed here.

The symbols used for the molecular constants are usually those which have been used by Herzberg in his well-known book "Molecular Spectra and Molecular Structure" Part I (1950).

ω_e, $\omega_e x_e$ and $\omega_e y_e$ are defined by

$$G(v) = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \omega_e y_e(v+\tfrac{1}{2})^3$$

r_e—internuclear distance at equilibrium

μ_A—reduced mass in atomic weight units

$k_e = 4\pi^2\mu c^2\omega_e^2 = 5.888 \times 10^{-2}\mu_A\ \omega_e^2$ dynes/cm.

D_0—dissociation energy for the ground state

( )—constants and symbols in parentheses are uncertain.

The new unit :

The force constant k_e is usually expressed in terms of 10^5 dynes/cm. It seems better to have some short symbol for this unit as the force cons tant is used very frequently. The authors suggest the symbol "Des", after-Deslandre, the pioneeer worker in Molecular Spectra. It is hoped that the suggestion will meet the approval of other workers in the field.

DATA

The data has been taken in most cases from the following sources :

1. G. Herzberg : "Molecular Spectra and Molecular Structure" Part I, 1950, (D. Van Nostrand Co. Inc., New York).

2. G. Herzberg : "Atomic Spectra and Atomic Structure", 1944 (Dover Publications, New York).

3. A. G. Gaydon : "Dissociation Energies and Spectra of Diatomic Molecules", 1950 (Dover Publications Inc., New York).

4. B. Rosen (editor) : "Donnees Spectroscopiques Concernant les Molecules Diatomiques", 1951 (Hermann and Cie, Depositaires, Paris V e)

5. W. Jevons : "Report on Band-Spectra of Diatomic Molecules" (Appendix II), 1932 (Cambridge University Press).

6. C. D. Hodgman (editor) : "Handbook of Chemistry and Physics", 1951 (Chemical Rubber Publishing Co., Ohio).

7. C. E. Moore : "Atomic Energy Levels", 1949 (Washington).

INTRODUCTION

Matuyama (1934) proposed that the logarithms of the ground state vibrational frequencies of diatoms XX formed of the same element were linear with the logarithms of the atomic weights of X for each group in the Periodic Table. The relation may be expressed as

$$\log \omega_e + p \log A = \text{a constant} \qquad \ldots (1)$$

where p is a constant (~ 1) for a given group. It was found however, that discrepancies occurred in the LL period, containing NaNa, PP, SS, ClCl. It may be added that this cannot hold for the different isotopes, because, for the isotopes k_e is constant *i.e.*

$$4\pi^2\frac{A}{2}c^2\omega_e^2 = \text{constant}$$

or,
$$\log \omega_e + \tfrac{1}{2}\log A = \text{constant}$$

while in (1), $p \sim 1$.

Clark (1937) modified the above relation as follows :

$$\log \omega_e = p - n \log 2Z \qquad \ldots (2)$$

where n and p are constants and $2Z$ is the number of extra-nuclear electrons (twice the nuclear charge) of XX. He showed that equation (2) was more successful than Matuyama's, though the anomalies persisted in LL period.

A similar relation is found to hold good if, instead of $2Z$, the effective charge Z_e, defined as follows, is used.

$$V=\frac{RZ_e^2}{n^2} \text{ or } Z_e^2=\frac{n^2V}{R}$$

where V is the ionisation potential of X, n the total quantum number of the valence electrons, and R the Rydberg constant. We can write the final relation as

$$\log \omega_e = g - h \log n^2V \qquad \ldots (3)$$

where g and h are constants for each group. The relationship is shown graphically figure 1. To avoid overlapping the ordinates of the points of the fourth in fifth groups have been decreased by .6. The values of the constants g and h for the various groups are given in Table I.

TABLE I

Group	g	h
I	4.0594	1.1349
IV	4.9401	1.0431
V	6.4827	1.7338
V and VII	5.2353	1.2015

The results are tabulated in Table II. $\omega_e(3)$ represents the values calculated from equation (3) and $\omega_e(2)$ from the Matuyma-Clark relation (2).

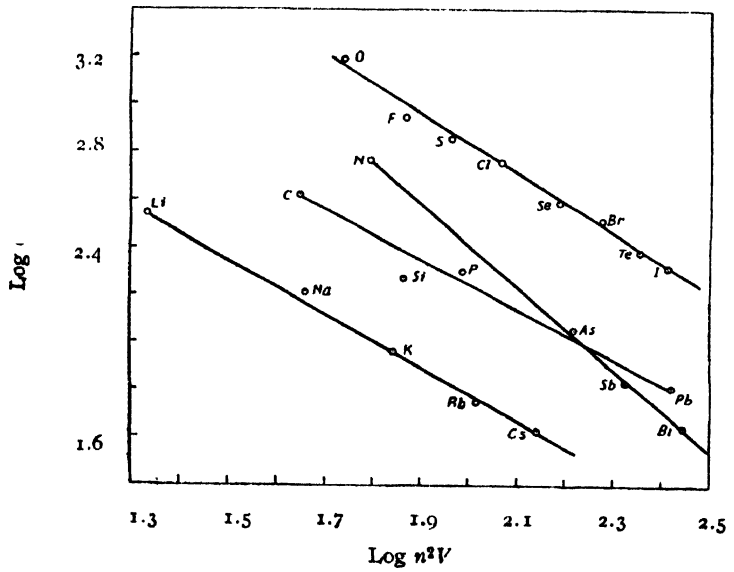

Fig. 1. The log ω_e values for the foltha nd fifth groups have been decreased by .6 to avoid overlapping

No experimental data for the ionisation potentials of Francium, Polonium and Astatine are available. However, Finkelnberg and Stern (1950) and Kohlrausch (1949) have estimated them by semi-empirical methods. The ionisation potential of Bi has been taken from Richtmyer and Kennard (1947). Other data have been taken from general references.

TABLE II

Group	Molecule	n	V in volt	$\omega_e(3)$	$\omega_e(2)$	ω_e observed
I	LiLi	2	5.390	351.4	351.4	351.4
	NaNa	3	5.138	147.9	136	159.2
	KK	4	4.34	93.1	91.2	92.6
	RbRb	5	4.176	58.6	56.1	57.3
	CsCs	6	3.893	42	42	42
	FrFr	7	4.0 ± 1[b]	30.7 ±1.2	30.1	
IV	CC	2	11.265	1641.3		1641.3
	SiSi	3	8.119	987		(750)
	GeGe	4	8.136	543		
	SnSn	5	7.332	380		
	PbPb	6	7.115	256.5		256.5
V	NN	2	15.545	2359.6	2359.6	2359.6
	PP	3	10.977	1057	1026	780.4
	AsAs	4	10.5	420.9	431.5	429.4
	SbSb	5	8.64	272.3	269.8	269.8
	BiBi	6	8.0[a]	165.3	157.4	172.7
VI	OO	2	13.615	1412	1580.4	1580.4
	SS	3	10.357	730.3	799.8	725.7
	SeSe	4	9.75	398.3	380.2	391.8
	TeTe	5	9.007	256.3	251	251
	PoPo	6	8.4 ± .3[b]	200.2 ±8.5	156.3	
VII	FF	2	17.422	1049	1080	(892)
	ClCl	3	12.959	565	604.5	564.9
	BrBr	4	11.844	316.3	312.9	323.2
	II	5	10.44	214.6	214.6	214.6
	AtAt	6	9.5 ± .2[b]	172.9 ±4.3	139.4	

a—Richtmyer and Kennard (1947)

b—Finkelnburg and Stern (1950). Kohlrausch's (1949) estimates for Fr, Po and At are 4.11, 8.3 and 9.4 respectively. Richter (1950) estimates 3.6 for francium.

DISCUSSION

It will be observed that the discrepancies in the LL period have been much reduced. While the calculated results for NaNa, SS, ClCl are satisfactory, there are still large errors in case of SiSi and PP. However, it must be remembered that the observed value of SiSi is uncertain, in as much as the identification of the bands as due to SiSi is tentative (Downie

and Barrow, 1947). It is also not certain that the lower state is the ground state. It is significant to note that there are strong vibrational and rotational perturbations in case of PP (Herzberg, 1932 ; Marais, 1946). The calculated value of OO is also much in error. The points for the VIth and VIIth groups are seen to lie on the same straight line. No determination of the ω_e for FrFr, GeGe, SnSn, PoPo and AtAt has been made. The predicted values are given in the table. The predicted value for FrFr is close to Clark's predicted value, but there is much difference for PoPo and AtAt.

ACKNOWLEDGMENT

The authors are thankful to the Council of Scientific and Industrial Research for the financial assistance and the permission to publish the results.

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